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Mass spectrometric study of molecular ions of methylphenol isomers using electron impact technique

Ezzat T M Selim, M A Fahmey and Hoda S Ghonime
Nuclear Physics Department, Nuclear Research Centre,
Atomic Energy Authority, Cairo, Egypt

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Abstract: The mass spectra of 2-, 3- and 4-methylphenol isomers at 70 and 14 eV have been recorded and discussed. Substituent effects of CH_3 and OH groups on the relative abundance of the prominent ions produced from melhylphenols as well as the mechanistic pathways for the formation of some major ions are reported and discussed. The ionization efficiency curves for the molecular ions of methylphenol isomers, using deconvoluted first differential technique are reported and investigated The values of ionization energies at threshold are measured at 8.46 ± 0.06, 8.36 ± 0.11 and 8.31 ± 0.08 eV for 2-, 3- and 4-methylphenol, respectively and are explained as due to ionization of $1e_{1g}$ electrons from $\pi_3(B_1$ component) orbitals of the corresponding methylphenol isomers. Molecular energy levels have been detected in the curves and some of these levels are tentatively explained.

Keywords: Mass spectra, methylphenol isomers, electron impact technique, substituent effects, ionization efficiency curves, molecular energy levels.

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1. Introduction

The abundance of the molecular ion, $[M]^+$, depends mainly on its stability and the amount of energy needed to ionize the molecule. Particular structural features tend to show characteristic values of these properties, so that the magnitude of $[M]^+$ provides an indication of the structure of the molecule (McLafferty 1973). On the other hand, the mass spectra of positional isomers are essentially similar, their spectra often exhibit differences in the relative abundances of some of the fragment ions (McLafferty 1973). However, some isomers could not be distinguished by electron impact mass spectra only because the relative intensities of the fragments are so similar (McIver 1975), therefore, it may be necessary to correlate between mass spectra and energy consideration.

The aim of the present work is to study the effect of the relative position of substituent groups CH_3 and OH on the relative abundance of the main fragment ions obtained from methylphenol isomers. Moreover, the ionization efficiency (IE)

curves for the molecular ions of methylphenol isomers (for about 4 eV above threshold) are reported using electron impact technique in order to measure the ionization energies and molecular energy levels for these isomers. It might be noted that valence shell orbital energies for the methylphenol isomers were investigated previously by Palmer *et al* (1979) using photoelectron spectra and *ab initio* MO calculation.

The directly measured IE data are treated with the deconvoluted first differential (DFD) technique (Selim 1985). The results (Selim and Helal 1982, Selim *et al* 1984, Selim 1985 and Selim *et al* 1987) obtained by this technique are reliable and sufficiently accurate for comparison with similar values in the literature.

2. Experimental

The IE curves were obtained using an Atlas CH-4 single focusing mass spectrometer with a normal electron impact (AN-4) ion source. The conditions of measurements and the method of calibration of the energy scale were the same as previously reported (Selim 1976). The electron energy was varied in 0.10 eV steps using a 10-turn helipot potentiometer and was measured with a digital multimeter Model VR-3511 of Hitachi. The energy scale was calibrated using the 15.76 eV threshold of argon.

The directly measured IE curves were smoothed using a 5-point smoothing (Savitzky and Golay 1964) computer technique in order to decrease the random noise in the raw data. Once again using a computer technique the smoothed data were treated to obtain the first derivative curves, and then the inverse convolution technique of Vogt and Pascual (1972) was applied to obtain the DFD IE curves. The complete details of the application of this combined technique had been reported elsewhere (Selim 1985) together with merits and limitations of the technique.

The mass spectra of methylphenol isomers were scanned at 70 and 14 eV electron energy and the intensity of prominent ions was calculated relative to the total ion intensity. Also, the metastable peaks associated with different fragmentation processes have been detected and reported.

3. Results and discussion

The mass spectra at 70 eV as well as 14 eV for the three molecules are recorded. Table 1 presents the relative intensities of the different peaks in the mass spectra of the three isomers relative to the total peaks intensity ($\%\sum_{70,14}$). The decomposition pathways for the formation of the principal ions obtained from methylphenol isomers are illustrated in Figure 1. The DFD IE curves (corrected) for $[C_7H_8O]^+$ molecular ions obtained from methylphenol isomers for about 4 eV above threshold are given in Figure 2. The values of ionization energies at threshold as well as molecular energy levels for the three isomers are reported in Table 2 together with

similar results reported previously by other authors using different techniques. The values reported in Table 2 are the average of six measurements and the errors quoted are the standard deviations. Only, reproducible values for molecular energy levels are reported in the Table.

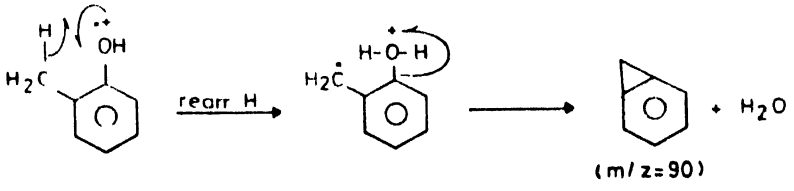
Table 1. Mass spectra of 2-, 3- and 4-methylphenol at 70 and 14 eV.

Ion formula	m/z	R.I*					
		2-methyl-phenol		3-methyl-phenol		4-methyl-phenol	
		70 eV	14 eV	70 eV	14 eV	70 eV	14 eV
$C_7H_8O^+$	108	30.03	63.5	29.22	62.77	29.08	60.53
$C_7H_7O^+$	107	22.60	23 1	25.07	25.3	28.85	27.72
$C_7H_6O^+$	106	0.72	—	0.76	—	0.81	—
$C_7H_6^+$	92	0.33	0.87	1.96	0.75	1.63	0.78
$C_7H_7^+$	91	2.51	2.16	3.42	2.45	3.08	2.42
$C_7H_8^+$	90	6.47	4.87	1.29	—	1.25	—
$C_7H_9^+$	89	2.18	0.63	0.2	—	0.35	—
$C_6H_8^+$	80	2.72	—	2.83	—	2.85	—
$C_6H_7^+$	79	7.84	3.37	7.48	4.52	7.59	5.38
$C_6H_6^+$	78	1.79	1.83	2.43	1.0	2.15	0.85
$C_6H_5^+$	77	7.15	2.54	6 93	2.57	7.33	2.30
$C_5H_5^+$	65	0.84	—	1.02	—	0.73	—
$C_5H_4^+$	64	0.45	—	0.56	—	0.52	—
$C_5H_3^+$	63	1.11	—	1.37	—	1.02	—
$C_4H_6^+$	54	1.38	—	1.49	—	1.39	—
$C_4H_5^+$	53	2.54	—	2.72	—	2.65	—
$C_4H_4^+$	52	1.59	—	1.72	—	1.80	—
$C_4H_3^+$	51	2.75	—	3.3	—	2.47	—
$C_4H_2^+$	50	1.71	—	1.78	—	1.28	—
$C_3H_3^+$	39	3.38	—	4.44	—	3.17	—

*The intensities are given as a percentage of total ion current from m/z = 39 up to the molecular ion ($\%\Sigma_{70,14}$).

1. Mass spectra of 2-, 3- and 4-methylphenol :

The relatively large peak at 70 eV and at 14 eV due to formation of $[M\text{-}H_2O]^+$ fragment ion (m/z=90) (Table 1) from 2-methylphenol, in comparison with relatively low intensity peaks for the same ion obtained from the other two isomers is an example of the "ortho effect" (McLafferty 1973).



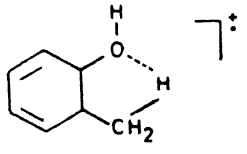
The $(C_7H_8O]^+_{\cdot}$ molecular ions obtained from the three isomers of methylphenol represent the most intense peaks in the presently measured mass spectra (base

Table 2. Ionization energies and molecular energy levels for 2-, 3- and 4-methylphenol molecular ions.

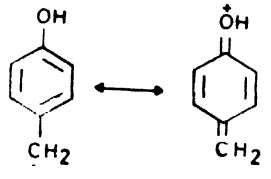
Ionization energies and molecular energy levels (eV)								
2-methylphenol			3-methylphenol			4-methylphenol		
This work	Literature		This work	Literature		This work	Literature	
	PES[a]	EI		PES[a]	EI		PES[a]	EI
8.46 ± 0.06	8 50	8.14[b], 8.93[e]	8.36 ± 0.11	8.41	8.23[b], 8.52 ± 0.05[c], 8.98[e]	8.31 ± 0.08	8.35	8 13[b], 8.34[d], 8.97[e]
9.40 ± 0.08	9.12		9.30 ± 0.16	9.14		9.29 ± 0.08	9.24	
10.36 ± 0.15	—		10.38 ± 0.15	—		10.23 ± 0.07	—	
11.20 ± 0.08	11.38		11.14 ± 0.08	11.18, 11.31		11.06 ± 0.09	11.12, 11.24	
11.76 ± 0.08	11.76		11.73 ± 0.09	11.74		11.56 ± 0.10	11.67	
12.39 ± 0.07	12.33		12.19 ± 0.09	12.40		12.61 ± 0.11	12.84	

(*a*) Palmer et *al* (1979); (*b*) Russell et *al* (1983); (c) Pignataro et *al* (1966); (*d*) Johnstone and Mellon (1973) and (e) Crable and Kearns (1962).

peaks) at 70 eV and 14 eV. The relative intensities of the ions are much higher at 14 eV than at 70 eV (Table 1) indicating a higher stability for molecular ions at the lower energy. The relatively higher stability of the molecular ion of 2-methylphenol (more intense peak) (Table 1) in comparison with the other two isomers, may be due to interaction between methyl group and oxygen atom (of OH group) as a result of proximity of the two groups which assists to increase the stability of the molecular ion of the 2-methylphenol more than in the case of the other two isomers. The bonding interaction may take the form :



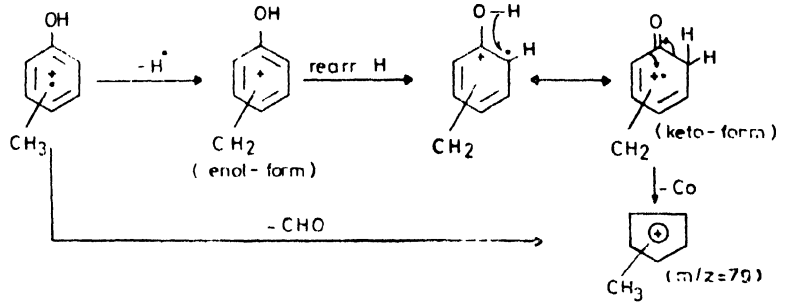
The $[C_7H_7O]^+$ ions represent the second most intense peaks in the mass spectra of the three isomers at the higher and the lower energies (Table 1). Labelling studies (Russell *et al* 1983) revealed that the loss of H occurs predominantly (70 %) at the methyl group. The order of decreasing intensity (stability) is 4-methylphenol > 3-methylphenol > 2-methylphenol. The relatively higher stability in case of 1, 4 position was discussed by Dewar and Landman (1977) as a result of strong interaction between the ring and hydroxyl group which is consistent with diquinoid structure. Also, they suggested that hydroxybenzyl ion may actually be more stable than hydroxytropylium structure. One may suggest the formation of diquinoid structure (Russell *et al* 1983) as :



The $[C_7H_7]^+$ fragment ions have a relatively low intensity in the mass spectra of methylphenol isomers at 70 eV as well as 14 eV (Table 1). The only possible way for forming $[C_7H_7]^+$ ions from methylphenols is the fracture of hydroxy-phenyl bond. As a result of the great stability of this bond [Aczel and Lumpkin (1960) discussed the great stability of phenol molecular ion as attributed to the resonance structure involving the unshared electrons on the oxygen atom], one expects that the probability for forming $[C_7H_7]^+$ ion will be minimized. The relatively lower intensity of $[C_7H_7]^+$ ion obtained from 2-methylphenol may be a result of interaction between methyl and hydroxyl groups as a result of proximity of the two groups which assists to increase further the stability of hydroxy-phenyl bond.

The $[C_6H_7]^+$ fragment ions are the third most intense peak in the mass spectra of methylphenol isomers. Two metastable peaks observed at 57.8 and

58.3 may indicate the formation of $[C_6H_7]^+$ ions from $[M]^+$ as well as $[C_7H_7O]^+$ ($[M-1]^+$) ions. The formation of $[C_6H_7]^+$ ions from $[C_7H_7O]^+$ ions (hydroxybenzyl structure) demands that the latter ions must be in a keto-form, while the formation of $[C_6H_7]^+$ ions directly from molecular ions of methylphenol isomers occurs by CHO loss from enol-form of molecular ion. The mechanisms of formation may be illustrated :



It is clear from the relative intensities at 70 eV and 14 eV (Table 1) that $[C_6H_7]^+$ ions formed from the three isomers at 70 eV have almost equal probability for formation, while at 14 eV a significant differences between the relative intensities of the ions produced from the three isomers are observed.

The $[C_6H_5]^+$ ions are the fourth most intense fragment ion in the mass spectra of methylphenol isomers. The relative intensities of the ions obtained from the isomers at 70 eV as well as 14 eV are almost equal.

Finally, the fragmentation pathways may be confirmed by the detection of metastable peaks in the mass spectra of the three isomers at m* equal to : 106, 58.3, 57.8, 75.05, 56.5, 55.4, 46.4, 34.7 and 33.8 (Figure 1) indicating

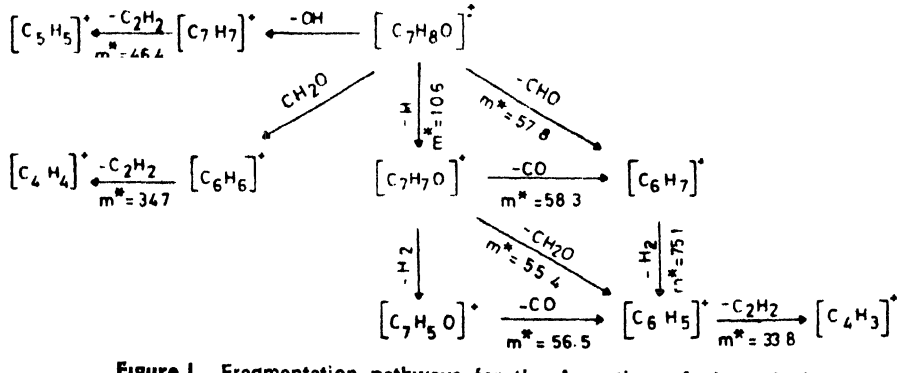


Figure 1. Fragmentation pathways for the formation of the principal ions obtained from methylphenol isomers.

similar fragmentation pathways, independent of the relative position of the OH and CH_3 substituents.

II. Molecular ions :

The three molecular ions under investigation in the present work are the isomeric molecular ions of methylphenol having the formula $[OH\text{-}C_6H_4\text{-}CH_3]^+$.

$[C_7H_8O]^+(m/z = 108)$ molecular ions obtained from 2-, 3- and 4-methylphenol :

The DFD IE curves for the molecular ions of 2-, 3- and 4-methylphenol show a slow rise (for about 1 eV above threshold) which may indicate that the adiabatic ionization energy does not coincide with vertical ionization energy. The ionization energies reported at threshold are 8.46 ± 0.06 eV (2-methylphenol), 8.36 ± 0.11 eV (3-methylphenol) and 8.31 ± 0.08 eV (4-methylphenol). The difference between the ionization energies of 2-methylphenol and 4-methylphenol is equal to 0.15 eV. This is in good agreement with the observation of Gibson (1973) that for disubstituted benzenes, the difference in ionization energies of the three isomers is less than 0.20 eV. The presently measured values of ionization energies of methylphenols at threshold are in good agreement with the first ionization energies of the same molecular ions measured by Palmer *et al* (1979) using photoelectron spectroscopy. The previously reported electron impact values by Russell

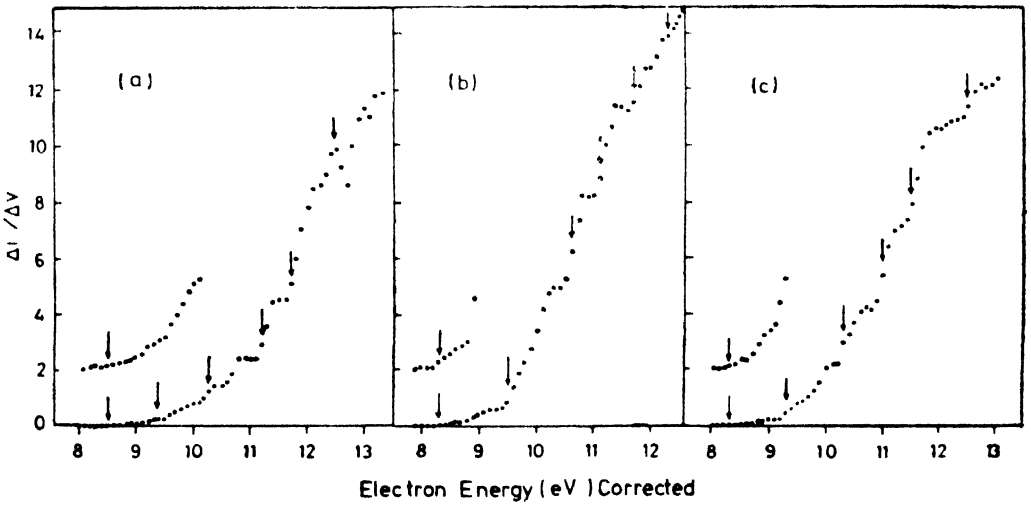


Figure 2. The deconvoluted first differential IE curves for $[C_7H_8O]^+$ (m/z=108) molecular ions obtained from (a) 2-methylphenol, (b) 3-methylphenol and (c) 4-methylphenol.

et al (1983) for the ionization energies at threshold of methylphenol isomers are lower than the presently measured values by 0.32, 0.13 and 0.18 eV for 2-, 3- and 4-methylphenol, respectively. The early reported electron impact values for the ionization energies by Crable and Kearns (1962) at 8.93 eV (2-methylphenol), 8.98 eV (3-methylphenol) and 8.97 eV (4-methylphenol) are very probably not corresponding to the first ionization energies of the three isomers. On the other hand, the ionization energy values at threshold measured by Pignataro *et al* (1966)

(8.52 eV) for the meta isomer and by Johnstone and Mellon (1973) (8.34 eV) for the para isomer using electron impact are in good agreement with the presently measured values. Recently, Mehler and Gerhards (1985) calculated the ionization energies and higher energy levels of the isomers of methylphenol by *ab initio* molecular-orbital calculations ; the calculated values are higher to high extent from the corresponding values measured in the present work.

Comparing the ionization energy at threshold for benzene (9.25 eV) (Palmer *et al* 1979) with that of phenol (8.56 eV) (Palmer *et al* 1979) and toluene (8.80 eV) (Selim *et al* 1982) indicates that the introduction of OH substituent in benzene lower the ionization energy of benzene by 0.69 eV while the introduction of CH_3 substituent lower the ionization energy by 0.45 eV. The additivity of substituent effects requires that the first ionization energy of benzene to be lowered by $0.69+0.45=1.14$ eV in case of the introduction of the OH and CH_3 substituents. However, the present results indicate that the ionization energies for methylphenol isomers at threshold are lowered relative to benzene by 0.79, 0.89 and 0.94 eV for 2-, 3- and 4-methylphenol, respectively.

One expects that the degeneracy of $^2E_{1g}$ ground state for benzene positive ion is removed (Dewar and Worley 1969) by the disubstitution of electron-donating groups ·OH and ·CH_3. Consequently, one may assume that the first ionization energies at 8.46, 8.36 and 8.31 eV for 2-, 3- and 4-methylphenol isomers, respectively are due to ionization of $1e_{1g}$ electrons from π_3 (B_1 component) orbitals of the corresponding methylphenol isomers. Hence the molecular energy levels measured at 9.40 eV (2-methylphenol), 9.30 eV (3-methylphenol) and 9.29 eV (4-methylphenol) are tentatively considered as due to ionization of $1e_{1g}$ electrons from π_2 (A_2 component) orbitals of methylphenol isomers.

The two lowest ionization energies of methylphenol isomers differ in energy by 0.94, 0.94 and 0.98 eV for 2-, 3- and 4-methylphenol, respectively. These almost equal differences which correspond to the splitting of π_3/π_2 orbital energy levels for methylphenols may be compared with differences 0.70 eV for phenol and 0.83 eV for anisole (Baker *et al* 1968). It is worthwhile to mention that the previous photoelectron spectroscopy results (Turner *et al* 1970) indicate that in disubstituted benzenes, where both substituents contribute to the moving apart of the π_2 and π_3 levels, the actual splittings are greater in the case of the para disubstituted compounds than in the corresponding ortho and meta derivatives.

Palmer *et al* (1979) had concluded, using *ab initio* MO calculations and photoelectron spectroscopy that the third ionization energy in 2- and 3-methylphenol is to be σ-orbital rather than π-type. On the other hand, they (Palmer *et al* 1979) considered the third ionization energy of 4-methylphenol to correspond to π-orbital. Following the conclusion of Palmer *et al* (1979) the present authors assume that the higher energy levels at 11.20 eV (2-methylphenol) and 11.14 eV (3-methylphenol) are due to removal of electron from the corresponding σ-orbitals. The higher energy level for 4-methylphenol at 11.06 eV is tentatively considered to be

due to one of the two lower π-electrons (a_{2u}). Palmer *et al* (1979) also measured a higher energy level at 11.31 eV in the photoelectron spectrum of 3-methylphenol and a similar one at 11.24 eV for 4-methylphenol. No equivalent levels have been detected in the presently reported ionization efficiency curves for 3- and 4-methylphenol.

Three higher molecular energy levels had been measured by us at 11.76 eV (2-methylphenol), 11.73 eV (3-methylphenol) and 11.56 eV (4-methylphenol). These levels have similarities to those reported by Palmer *et al* (1979) at 11.76 eV, 11.74 eV and 11.67 eV for 2-, 3- and 4-methylphenol, respectively and explained by them as due to removal of an electron from the corresponding π, σ and σ orbitals, respectively.

The molecular energy levels measured by the present authors at 12.39 eV (2-methylphenol), 12.19 eV (3-methylphenol) and 12.61 eV (4-methylphenol) have similar levels reported by Palmer *et al* (1979) using photoelectron spectroscopy technique at 12.33 eV, 12.40 eV and 12.84 eV for 2-, 3- and 4-methylphenol, respectively. Palmer *et al* (1979) had assigned the latter energy levels to removal of an electron from the corresponding σ orbitals for methylphenol isomers.

Finally, molecular energy levels have been measured at 10.36 eV (2-methylphenol), 10.38 eV (3-methylphenol) and 10.23 eV (4-methylphenol). No equivalent levels were reported in the literature using either photoelectron spectroscopy or electron impact techniques.

References

Aczel T and Lumpkin H E 1960 *Anal. Chem.* **33** 386

Baker A D, May D P and Turner D W 1968 *J. Chem. Soc. (B)* **22**

Crable G F and Kearns G L 1962 *J. Phys. Chem.* **66** 436

Dewar M J S and Worley S D 1969 *J. Chem. Phys.* **50** 654

Dewar M J S and Landman D 1977 *J. Am. Chem. Soc.* **99** 4633, 7439

Gibson H W 1973 *Can. J. Chem.* **51** 3065

Johnstone R A W and Mellon F A 1973 *J. Chem. Soc. Faraday Trans. II* **69** 36

McIver (Jr) R T 1975 *Org. Mass Spectrom.* **10** 396

Mehler E L and Gerhards J 1985 *J. Am. Chem. Soc.* **107** 5856

McLafferty F W 1973 *Interpretation of mass spectra* (Benjamin : London)

Palmer M H, Moyes W and Speirs M 1979 *J. Mol. Struct.* **52** 293

Pignataro S, Foffani A, Innorta G and Distefano G 1966 *Z. Phys. Chem.* (Frankfurt) Neue Folge, Bd **49** 291

Russell D H, Freiser B S, McBay E H and Canada D C 1983 *Org. Mass Spectrom.* **18** 474

Savitzky A and Golay M J E 1964 *Anal. Chem.* **36** 1627

Selim E T M 1976 *Indian J. Pure Appl. Phys.* **14** 547

1985 *Egypt. J. Phys.* **16** 249

Selim E T M and Helal A I 1982 *Org. Mass Spectrom.* **17** 539

Selim E T M, Helal A I and Zahran N F 1984 *Proc. Indian Acad. Sci. (Chem. Sci.)* **93** 87

Selim E T M, Rabbih M A, Fahmey M A and Rezk A M H 1987 *Org. Mass Spectrom.* **22** 381

Turner D W, Baker C, Baker A D and Brundle C R 1970 *Molecular photoelectron spectroscopy* (London : Wiley Interscience)

Vogt J and Pascual C 1972 *Int. J. Mass Spectrom. Ion Phys.* **9** 441